FORMATION OF DIAMOND WHISKERS BY RF PLASMA ETCHING

C.Y. Li and A. Hatta

Department of Electronic and Photonic Systems Engineering, Kochi University of Technology,
185 Miyanokuchi, Tosayamada-cho, Kami-gun, Kochi 782-8502, Japan

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Abstract

Diamond whiskers were fabricated by means of radio frequency plasma etching. Metal particles were coated onto diamond films to serve as micro-masks before etching. Etching processing was performed using O_2/Ar plasmas, with an emphasis to elucidate the effects of reacting gas on the fabrication of diamond whiskers. The results showed that the densities and the distributions of diamond whiskers depended on the volumetric ratio of O_2 to Ar. Raman spectroscopy was carried out in order to determine the bonding structures of the whiskers. It has been found that the whiskers were still diamond after etching. X-ray photoelectron spectroscopy was carried out to investigate the components of diamond surface after etching. Field emission characteristics of the whiskers were also inspected.

I. INTRODUCTION

Diamond films are attractive to applications in cathode electron field emission devices [1]. It was reported that the electron field emission would be enhanced at the micro-tips of diamond [2]. Among the various approaches for fabrication of sharper field emission tips, reactive ion etching (RIE) in radio frequency (RF) plasmas is considered as an efficient method to sharpen diamond micro-rods [3]. In this paper, a novel method for fabrication of whiskers in O_2/Ar plasmas was reported. A comparison of the morphologies of diamond surfaces before and after etchings demonstrated that the properties of whiskers were dependent on the reacting gas, respectively.

2. EXPERIMENT DETAILS

Polycrystalline diamond films were deposited onto Si substrates using a microwave plasma chemical vapor deposition (PCVD) reactor system ASTeX (AX-6350). The deposition process was carried out under pressure of 124 torr, microwave power of 5 kW, and flow rates of 25 and 475 sccm for CH_4 and H_2, respectively. During the deposition, the substrate temperature was kept at 900-950 ℃, monitored by a spot thermometer. The diamond films were coated using metal particles after growing to 3 μm in thickness. The etching process was performed for 60 min in a self-assembled RF plasma reactor with frequency of 13.56 MHz. The chamber pressure was maintained at 22 Pa. Reacting gases were introduced through a mass flow controller. The RF power was 100 W, corresponding to a DC self-bias voltage of -510 V. In this study, the gas compositions examined were O_2 (10 sccm)/Ar (90 sccm), O_2 (20 sccm)/Ar (35 sccm), O_2 (100 sccm), and Ar (100 sccm).

3. RESULTS AND DISCUSSION

Figure 1 presented the SEM images of the diamond surfaces after etching. Whiskers were found on the surfaces of the samples. An interesting phenomenon was that the distribution of whiskers was not random. For etching in O_2/Ar plasma with 10% O_2 (vol/vol), whiskers with 150 nm diameter and 200 nm height formed only at the grain boundaries, suggesting that the whiskers might form preferentially at the grain boundaries between diamond crystals [4]. However, with increasing O_2 concentration (O_2: 36%), the whiskers extended gradually into the diamond grains. It could be noticed that the height of the whiskers remarkably increased to 900 nm. When the O_2 ratio approached to 100%, the whiskers had the highest density ($40/\mu m^{-2}$). The average diameter of the whiskers reduced to 100 nm with a height of 1 μm. In inert gas Ar (100 sccm), whiskers could not be formed on the surfaces after etching.

In general, there were two processes during the RF plasma etching [5]. Inert gas plasma only caused physical bombardment etching which could explain why whiskers could not be obtained in pure Ar. However, the etching process was different in Ar and O_2 mixture plasmas. Whiskers obtained in the latter could be ascribed to the processes of ion-enhanced chemical etching and physical bombardment etching. O_2 would dissociate into O radicals accompanied by the formation of volatile products of CO and CO_2, while Ar would contribute to bombarding the diamond surfaces. [6,7].

All of above suggested that the density and height of whiskers increased with increasing flow ratio of O_2 to Ar. It is conceivable that the formation of whiskers could be controlled by changing the concentration of O_2 in the reacting gas.

The metal masks were also critical to the erosion of diamond films. In this experiment,Al was masked on the diamond surfaces before etching, it would react with O_2 to form Al_2O_3 islands on the tops of the whiskers, inhibiting the etching underneath [8,9]. Thus, the distribution of whiskers might be controlled by masking metals on the diamond surfaces. The remains of metal particles on the tops of whiskers were examined by XPS.

In order to determine the structures of whiskers, Raman spectroscopy was performed for samples before and after etchings. In Fig.2, the Raman spectrum showed a diamond (sp^3 bonding) peak at 1331 cm^{-1} along with a low broad non-diamond (sp^2 bonding) peak at 1580 cm^{-1}. The presence of a weak graphite peak might be attributed to a small amount of local transformation from sp^3 to sp^2. Most of the bonding structures were kept on sp^3 diamond structures during etching process. Therefore, we could conclude that the whiskers were still diamond after etching.

Samples after etching were treated in hydrogen plasma for 8 min before field emission measurement. A turn-on field of 10 V/μm was obtained for the whiskers etched in pure O_2 plasma.

4. CONCLUSION

Reactive ion etching in RF plasmas is an effective method to obtain diamond whiskers. The densities and the distributions of whiskers could be controlled by adjusting the volumetric ratio of O_2 to Ar and by means of appropriate metal masks. There were few changes in the bonding structures of the whiskers, and the diamond structures remained unchanged after etching. The turn-on field of the whiskers was as low as 10 V/μm. Therefore, it is possible to use whiskers to cathode emission devices.

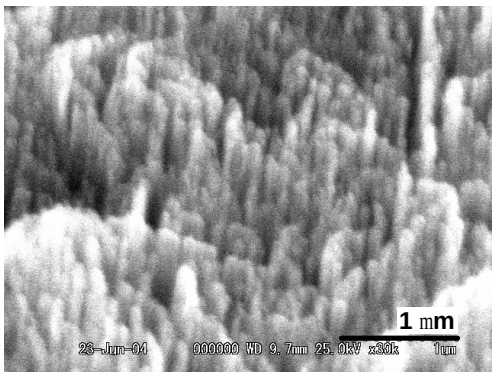

Fig.1. SEM images of diamond whiskers obtained from etching in O_2 (100 sccm).

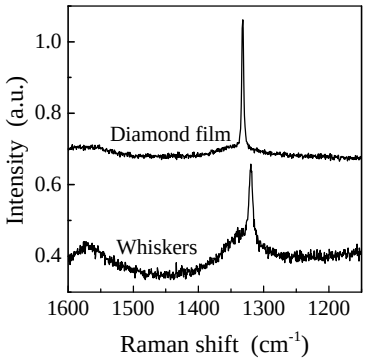

Fig.2. Raman spectra for the diamond film and the whiskers (Al coated, O_2 100 sccm, etched 60 min).

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